

Theory of photoferroelectric response in SmC* liquids

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We are concerned with the modification of liquid crystalline and polar order in SmC* liquids by illumination. In particular we show that non-uniformity due to absorption and also dynamics, can be complex. The variation of polarization with temperature, while illuminated, is modified from that assuming uniformity. Apparent changes of polarization with illumination will be shown to be underestimated due to non-uniformity. The dynamics is shown to depend on propagating fronts of photo-conversion penetrating the sample.

I. INTRODUCTION

Smectic C liquids possess an underlying nematic, or orientational ordering of their molecular rods. Additionally the rods have some ordering into layers, with layer normal \mathbf{k} , and their nematic director \mathbf{n} is tilted by an angle θ with respect to \mathbf{k} (Fig. 1).

When the rods are chiral we have a SmC* liquid where the plane of \mathbf{k} and \mathbf{n} is no longer a mirror plane. As first recognized by Meyer¹, a SmC* admits a spontaneous polarization along $\mathbf{k} \wedge \mathbf{n}$, that is in the layers and perpendicular to \mathbf{n} and \mathbf{k} . Indeed Pikin and Indenbom² pointed out that $(\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \wedge \mathbf{k})$ is the appropriate order parameter and that the polarization, \mathbf{P}_s , can be expressed as

$$\mathbf{P}_s = \varepsilon_0 \chi_0 c^* (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \wedge \mathbf{k}), \quad P_s = \varepsilon_0 \chi_0 c^* \theta, \quad (1)$$

where ε_0 is the standard vacuum permittivity, χ_0 is the generalized susceptibility of a corresponding racemate in the direction perpendicular to \mathbf{n} and \mathbf{k} , and c^* is the so-called bilinear coupling coefficient. The latter expression

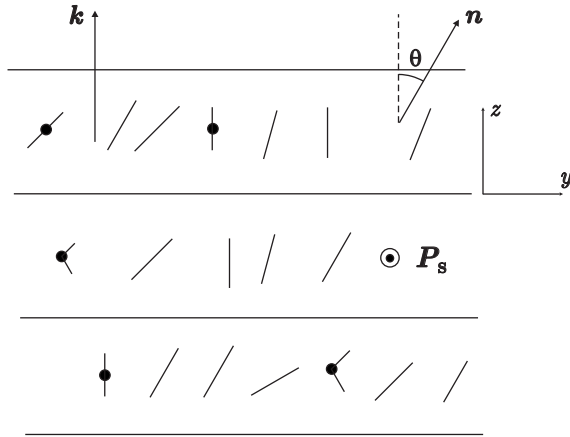


FIG. 1. A smectic C* liquid host. Guest dye molecules with a photo-active center indicated by a dot are also shown, some in their linear (*trans*) ground state, others bent, in their excited (*cis*) state.

for P_s holds for small tilt (see Lagerwall's book³ for a review; we adopt his convention for the coupling c^* , with an asterisk indicating its chiral origin). The polarization is termed “pseudo proper ferroelectricity” since the primary order parameter is not the polarization but derives from the tilt which in turn drives the polarization.

On increasing temperature, the SmC* phase undergoes a second-order phase transition to the SmA* phase. The tilt angle θ of the SmC* phase vanishes near the critical temperature T_{AC} , and consequentially P_s too. It is expected that this transition belongs to $d = 3$, $n = 2$ universality class⁴.

It has been long known that the order can be changed by irradiation of SmC* containing photo-active rods as guests⁵⁻⁹. By absorbing a photon dye molecules can make transitions from the ground (*trans*) state to the excited bend-shaped (*cis*) state. The molecules in the *cis* state either disrupt the SmC* ordering to change θ , at a given T , or weaken the coupling c^* . Both changes are a route to changing P_s , hence the name photoferroelectric effect. Langhoff and Giesselmann were concerned with attributing photo changes to primary (c^*) or secondary (θ) influences¹⁰.

We are concerned with the character of the light absorption. Since there has to be a finite change in the ground state population of absorbers, then the absorption can not be linear, that is it must be non-Beer in form. Moreover the detailed dynamics of P_s and θ observed after the start of illumination indicates nonlinear effects. In any event, polarization is likely to vary pronouncedly with depth into the sample, especially away from T_{AC} and at not too high intensities of incident light. We show how to accommodate this non-uniformity in modeling the photo response. We suggest experiments to correlate P_s with mechanisms of absorption.

We first sketch in Sect. II the forms of light absorption leading to non-uniform polarization. We then present a simplest model of how to translate the dark state polarization into the light state, and superimpose such results to model experiment. In Sect. III we introduce dynamics to construct the analogous time-dependent forms of the measured polarization. Switch-on dynamics depends on propagating fronts of photo-conversion penetrating the sample, while switch-off dynamics is essentially a relaxation type dynamics.

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II. LIGHT ABSORPTION AND NON-UNIFORMITY OF PHOTO-CONVERSION

A. Light absorption

The intensity, I , of light varies with depth, x , due to absorption by *trans*-species of dye molecules

$$\frac{\partial I}{\partial x} = -\gamma \Gamma I(x, t) n_t(x, t), \quad (2)$$

where Γ is a rate coefficient for photon absorption and $\gamma = \hbar \omega n_d$ subsumes the energy $\hbar \omega$ of each absorption of a photon from the beam and the absolute number density of chromophores, n_d . The number fraction of these chromophores in their *trans* state is n_t ; clearly $n_t + n_c = 1$, where n_c is the number fraction of chromophores in the *cis* state. To simplify dynamics we neglected absorption by the *cis*-species. This can be justified by the fact that most experiments performed so far used light wavelengths in the vicinity of the *trans* absorption maximum. We normalize $I(x, t)$ by the incident intensity I_0 to give an $\mathcal{I}(x, t) = I(x, t)/I_0$. The combination $\gamma \Gamma$ will be written $1/d_B$ with d_B the Beer length. Eq. (2) can be rewritten as

$$\frac{\partial \mathcal{I}}{\partial x} = -\frac{n_t}{d_B} \mathcal{I}. \quad (3)$$

If the *trans*-population of absorbers is assumed to change little, $n_t(x, t) \simeq 1$, then one has Beer attenuation $\mathcal{I} = e^{-x/d_B}$. Only if the sample thickness, L , is much less than d_B do we obtain a roughly uniform response, though in the Beer limit we assume essentially no response, $n_t \simeq 1$. Eq. (3) can only be closed if we know the *trans*-population at (x, t) . We have

$$\frac{\partial n_t}{\partial t} = -\eta \Gamma I(x, t) n_t + \frac{n_c(x, t)}{\tau}, \quad (4)$$

where changes in n_t are due to conversions, with quantum efficiency η per photon absorption of *trans-cis* transition, and thermal back reaction from *cis*-population at a rate $1/\tau$, with τ the *cis* lifetime. In the steady state, $\partial n_t / \partial t = 0$, we have

$$n_t(x) = \frac{1}{1 + \alpha \mathcal{I}}. \quad (5)$$

We adopt the convention: where the t argument is absent, we are denoting the steady state values of n_t and \mathcal{I} . The combination $\alpha = \eta \tau \Gamma I_0 \equiv I_0/I_t$ is a measure of how intense the incident beam is compared with a material constant I_t for the *trans* species. The parameter α is a balance between the forward rate, $\eta \Gamma I_0$, and the back rate, $1/\tau$. The solution of Eq. (3) in the equilibrium case can be obtained by using relation (5)

$$\ln[\mathcal{I}(x)] + \alpha[\mathcal{I}(x) - 1] = -\frac{x}{d_B}. \quad (6)$$

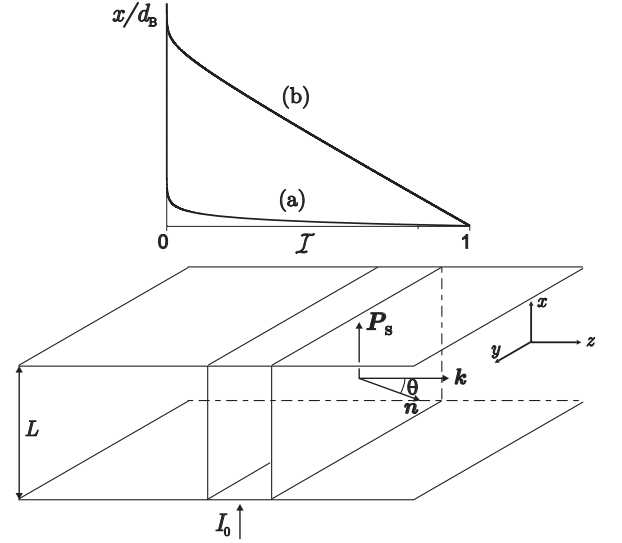


FIG. 2. A SmC* sample between two electrodes illuminated from below ($x = 0$) with light of intensity I_0 . The decay of scaled intensity $\mathcal{I}(x) = I(x)/I_0$ is shown above: (a) exponential (Beer) decay, $\alpha = 0$; (b) deep penetration (non-Beer), in this example $\alpha = 30$.

For $\alpha = 0$, we have the usual exponential form of Beers law. For large α we have linear rather than exponential penetration

$$\mathcal{I}(x) \simeq 1 - \frac{x}{\alpha d_B} \quad (7)$$

at least over depths up to $x \sim \alpha d_B$ whereupon \mathcal{I} is small and the $\ln(\mathcal{I})$ again prevails to give a finally exponential penetration (see curves (a) and (b) in Fig. 2 for examples of both profiles). Thus, depletion of the absorber population at high intensities can give very deep penetration to $x \gg d_B$. Non-Beer absorption was first explored for dyes in liquid crystals (nematics) by Statman and Janossi¹¹ and by Corbett and Warner^{12,13}. The determinant, α , of whether the absorption is non-linear depends on temperature T since the *cis-trans* decay is activated. The excited state thermal life time takes an Arrhenius form $\tau = \tau_0 e^{\kappa/T}$. We shall require $n_c(x, \alpha)$ as a function of T which enters through $\alpha(T)$.

B. Irradiation as a form of dilution

When suitable dye molecules absorb a photon they bend (photoisomerize) and thereby weaken the ordering potentials causing the underlying nematic order, the tilt and the hindered rotation about the molecular axis that ultimately gives the electric polarization in SmC* liquid crystals. The first two orderings strengthen the latter. One might imagine that for the soft interactions, giving thermal effects (in contrast to the athermal effects of hard, steric packing), there are effective potentials and

hence probabilities of the form

$$p(\psi) \propto \exp\left(-\frac{Jf(\psi)}{k_B T}\right), \quad (8)$$

where $f(\psi)$ is a function of some suitable generalized coordinate ψ , and J is a scale to the coupling interaction. We further assume that J scales according to $J = J_0(1 - \delta + n_t \delta)$, which suggests that as neighboring molecules in a coordination shell are bent, $n_t < 1$, they contribute less or not at all to the ordering; here J_0 stands for interaction strength in the dark. The fraction of molecules present that are photo-active is δ . Here $\delta \sim 0.05$ in the guest-host systems of Langhoff and Giesselmann^{10,14} and $\delta = 1$ in the pure systems of SmC* photo-rods¹⁵. The fraction δ would perhaps be smaller than its purely number fraction value because dye molecules converted from *trans* to *cis* state still contribute to some extent to the ordering (residual *cis*-effect). Rearranging via $n_t = 1 - n_c$, we obtain $J = J_0(1 - \delta + n_t \delta) = J_0(1 - n_c \delta)$. Overall, we can write the coupling strength relative to thermal effects in Eq. (8) as

$$\frac{J_0}{k_B T / (1 - n_c(x) \delta)} \Rightarrow T \rightarrow \frac{T}{1 - n_c(x) \delta}. \quad (9)$$

The latter is the effective rise in temperature mapping to a particular illumination, $\mathcal{I}(x)$, that determines $n_c(x)$.

C. Interpretation of measurements of non-uniform $P_s(x)$

Commonly, spontaneous polarization is measured by applying a triangular voltage¹⁶ across a cell filled with SmC* liquid crystal; see Fig. 2. On reversing this voltage, the polarization also reverses leading to a flow of polarization charge. We leave aside the question whether the system in the field-free state is helical, surface stabilized¹⁷ or in the **V**-switching state with \mathbf{P}_s in the (x, y) plane; see Čopič *et al.*¹⁸ for the underlying physics. Langhoff and Giesselmann do not specify which their systems are, but they have samples of thickness $L = 2 \mu\text{m}$ so a helical ground state is unlikely.

Taking into account that *cis* concentration varies with depth, it is clear that spontaneous polarization should be non-uniform. The polarization perceived to be switched is

$$\begin{aligned} \overline{P}_s(T, I_0) &= \frac{1}{L} \int_0^L dx P_s(T, x) \\ &= \frac{1}{L} \int_0^L dx P_s^0 \left(\frac{T}{1 - n_c(x) \delta} \right), \end{aligned} \quad (10)$$

where $P_s(T, x)$ is the actual polarization at depth x . By contrast $P_s^0(T/(1 - n_c \delta))$ is our model of polarization at x , namely the dark-state polarization but shifted to higher effective temperatures if $n_c(x) > 0$. We apply our model of dilution simply to polarization, leaving aside the question of tilt angle.

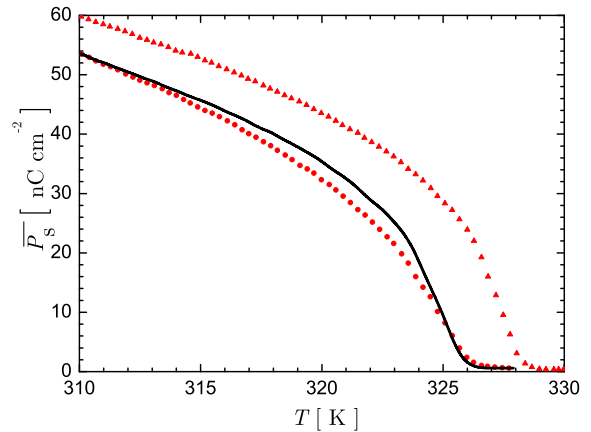


FIG. 3. Spontaneous polarization as a function of temperature calculated by using relation (10), as explained in the main text, for the values of fitting parameters $\delta = 0.019$, $\tau_0 = 27.76 \times 10^{-12}$ s and $\kappa = 9765$ K (solid line). For comparison, we have shown experimental results in the irradiated state (circles). Experimental results for the dark state (triangles), which we used as an input to obtain our curve, are also presented.

Ideally the aim of experiment is to measure photo-induced depression of the dark state polarization $P_s^0(T)$ to the value $P_s(T, I_0)$ characteristic of the incident intensity. However, in a real measurement, the depression to $P_s(T, I_0)$ only takes place at the incidence surface, and is less deeper in the sample since the intensity drops; $I(x) < I_0$. Being a depth average, $\overline{P}_s(T, I_0)$ is depressed less than the depression to $P_s(T, I_0)$. Thus the measured change is an underestimate of that suffered by a system uniformly exposed to I_0 .

D. Comparison with experiment

To test the above modeling strategy, we take Langhoff and Giesselmann's¹⁰ dark-state $P_s^0(T)$ and match it to photo-modifications they obtain. Since a field is applied to measure polarization by its reversal, the dark-state $P_s^0(T)$ clearly has a foot for $T > T_{AC}$ (due to the electroclinic effect where tilt is induced by a field¹⁹) and is also modified for $T < T_{AC}$ away from any singular, zero field result (see Fig. 3).

At finite incident illumination, I_0 , the fit to the experimental $\overline{P}_s(T, I_0)$ of Eq. (10) is good (Fig. 3). Since the characteristics of the absorption, d_B and α , are not available, we have estimated $d_B = 3.2 \mu\text{m}$ from the known absorption of azobenzene²⁰, but adjusted for the different molecular number densities of azobenzene and the dye used by Langhoff and Giesselmann. Some factors entering the parameter $\alpha = \eta I_0 \Gamma \tau = I_0 \eta \tau / \gamma d_B$ are taken from experiment ($I_0 = 75 \mu\text{W cm}^{-2}$ and $\lambda = 365$ nm), while some of them can be estimated (η and γ). For in-

stance the quantum efficiency can be taken²¹ as $\eta \simeq 0.6$ in these azo-based dyes and $\gamma = \hbar\omega n_d = 5.4 \times 10^7 \text{ J m}^{-3}$. Still, we have two free parameters, τ_0 and κ , entering α through $\tau = \tau_0 e^{\kappa/T}$. In addition, we use δ as a third fitting parameter. This parameter is a measure of how much ordering influence of a dye molecule is lost when it is transformed to the *cis* state, and is therefore expected to be different from the bare dye number fraction 5%. Thus three fitting parameters remain at our disposition. The best overall fit presented in Fig. 3, we obtained with the following values of fit parameters: $\delta = 0.019$, $\tau_0 = 27.76 \times 10^{-12} \text{ s}$ and $\kappa = 9765 \text{ K}$. In our analysis, the parameter $\alpha(T)$ changes in the range (0.67, 3.46) which corresponds to the nonlinear (i.e. non-Beer) absorption regime. The departure of $\overline{P}_s(T, I_0)$ from the data at lower temperatures is perhaps a measure of the athermal (packing) effects mentioned above. Future experiments could measure absorption characteristics d_B and $\alpha(T)$ and thus reduce the number of fit parameters to only one – our δ .

E. Analysis of pure dye systems

Examination of the experimental $\overline{P}_s(T, I_0) - T$ curves shows that for a given I_0 there are temperatures at which the polarization is uniform through the thickness, namely $P_s(T, x) = 0$ since the average \overline{P}_s that is measured vanishes. At all lower temperatures the polarization profile must be non-uniform. One can draw a quite powerful conclusion from this observation. In the experiments we quoted in the previous section the number fraction of dye molecules was 5%. Given that there is still a profile of light intensity and hence also of $n_c(x)$, even when $P_s(T, x) = 0$ for all x between 0 and L , then P_s must be vanishing at the back face when $n_c < 1$ and hence an "impurity" level of less than 5% is sufficient to eliminate P_s .

The low level of required molecular transformation to achieve the maximal polarization change suggests a possible explanation of the perplexing results of Saipa *et al.*¹⁵. These authors found that the greatest photo-induced changes of polarization occurred for irradiation at a wavelength $\lambda = 450 \text{ nm}$, near the *cis* absorption maximum, rather than at $\lambda \simeq 360 \text{ nm}$, the *trans* absorption maximum where conversion is most likely and naively polarization reduction would be most efficient. Their system was composed 100% of the dye W470 with a huge dark state polarization of up to 230 nC cm^{-2} . In a 100% dye system, irradiated with light of wavelength $\lambda \simeq 360 \text{ nm}$, the Beer length is short, presumably $d_B \ll L$. Then at low intensities conversion to *cis* is in a thin layer $\sim d_B$. This localization of conversion means that $\overline{P}_s \sim (1 - d_B/L)P_s^0$, that is the change in average polarization is very little. To convert over a greater depth, and therefore to get a greater depression of \overline{P}_s , one has to increase the incident intensity, that is, α . Then the conversion in the initial layers must be to a significant $n_c \lesssim 1$

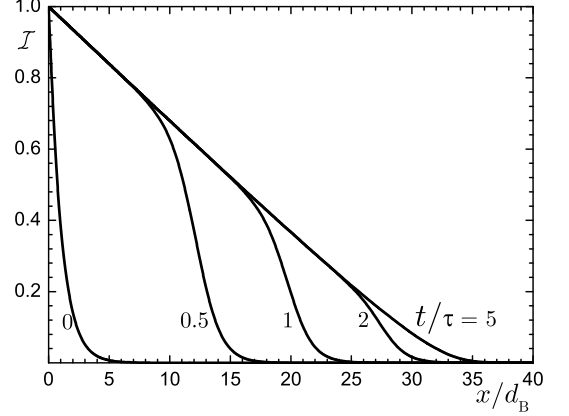


FIG. 4. Reduced intensity $\mathcal{I} = I/I_0$ as a function of reduced depth x/d_B for $\alpha = 30$ and different reduced times $t/\tau = 0, 0.5, 1, 2$ and 5 .

in order to eliminate absorbers (*trans* isomers) from the path. Then the average $\overline{P}_s \rightarrow 0$ since conversion deeper down can take place. However, this strategy is very inefficient since significant volumes of the sample have $n_c \sim 1$ rather than $n_c \sim 0.05$ or less that we have seen is already adequate to obtain complete loss of P_s . Far more effective in this experiment was to have light well de-tuned from the *trans* to *cis* absorption maximum. Thus, conversion was lower, but perhaps sufficient to achieve $P_s(T, x) = 0$, and light being de-tuned penetration was deeper. Then there would be a greater volume with $P_s = 0$, and thus a greater change in \overline{P}_s . However, this is an inefficient way to proceed since much *cis* absorption of photons also takes place.

III. DYNAMICS

Since the depression of polarization rests upon the number fraction n_c of *cis* molecules, the dynamics of $\overline{P}_s(T, I_0, t)$ is specified by the dynamics of $n_c(x, t)$ which we now sketch.

Beer absorption strictly has no dynamics since it holds only if the number fraction n_t is unchanging; $\partial \mathcal{I} / \partial x = -\mathcal{I} / d_B$. Equally, there could be no change in P_s since $n_c = 0$ in this limit. To explore the dynamics of non-Beer absorption, we need to solve the coupled Eqs. (3) and (4). It can be shown²² that these simultaneous, nonlinear partial differential equations can be reduced to a quadrature

$$\frac{t}{\tau} = \int_{\mathcal{A}}^{x/d_B} \frac{d\mathcal{A}'}{\alpha + \mathcal{A}' - x/d_B - \alpha e^{-\mathcal{A}'}} \quad (11)$$

where $\mathcal{A} = -\ln(\mathcal{I})$ is the absorption (here logs base e). At $t = 0$, before any conversion has had time to deplete the (*trans*) absorbers, $n_t = 1$ and $\partial \mathcal{I} / \partial x = -\mathcal{I} / d_B$

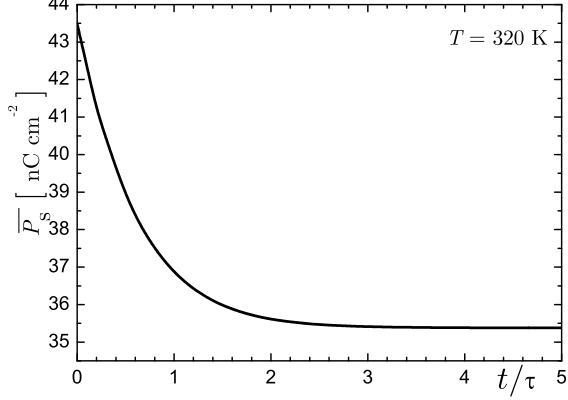


FIG. 5. Spontaneous polarization (12) as a function of reduced time t/τ for $T = 320$ K and the values of δ , τ_0 and κ as in Fig. 3.

simply; the $\mathcal{I}(x, t = 0)$ profile is of the Beer form and $\mathcal{A}_B = x/d_B$. The lower limit tends to the upper causing the integral to vanish and thus $t/\tau = 0$, as required. For $\mathcal{A} \rightarrow \mathcal{A}_{eq}$, the equilibrium nonlinear (non-Beer) absorbance, the integral diverges since Eq. (6) for \mathcal{A}_{eq} is nothing other than the vanishing of the denominator in Eq. (11) – hence $t/\tau \rightarrow \infty$. From the solution $\mathcal{A}(x/d_B, t/\tau)$ of (11) we obtain $\mathcal{I} = e^{-\mathcal{A}}$. This nonlinear absorption dynamics has been thoroughly verified by the experiments of Serra and Terentjev²³. As time increases, and for intense enough beams ($\alpha \gtrsim 1$), depletion of $n_t(x, t)$ means greater penetration of \mathcal{I} . In effect a front of conversion penetrates the sample giving a growing volume where $P_s(T, x, t)$ is depressed; see Fig. 4.

Armed with $\mathcal{A}(x, t)$, we have $n_t = d_B \partial \mathcal{A} / \partial x$ on rearranging (3), and hence $n_c = 1 - n_t$ which generalizes Eq. (10) to the time-dependent polarization

$$\overline{P}_s(T, I_0, t) = \frac{1}{L} \int_0^L dx P_s^0 \left(\frac{T}{1 - n_c(x, t)\delta} \right). \quad (12)$$

Fig. 5 shows how the measured polarization is depressed by illumination only as a front of conversion to *cis* advances through the sample thickness.

The switch-on dynamics generally takes place over a period $t \lesssim \tau$, depending on the incident intensity, I_0 , that is on α , and on the thickness L/d_B for the conversion front to propagate through; see Fig. 2 of [22] where this is demonstrated for a range of thicknesses and incident light intensities. The characteristic on-time approaches τ for thicker samples where $L/d_B \sim \alpha$.

Switch-off dynamics is driven by the response \dot{n}_t of (4) when $I = 0$, that is

$$n_c(x, t) = n_c(x, 0)e^{-t/\tau}, \quad (13)$$

where now t is the time since switch-off. The $n_c(x, 0)$ number fraction at that time could either be the equilib-

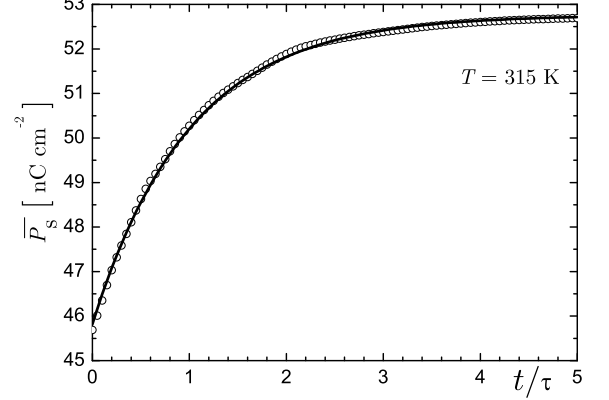


FIG. 6. Polarization versus reduced time for $T = 315$ K and the values of δ , τ_0 and κ as in Fig. 3. The "exact" data, i.e. those obtained by using the integration procedure indicated by formula (12) are presented by circles, while the solid curve represents the fit to the monoexponential curve $A + Be^{-t/\tau}$, where τ is the thermal relaxation time τ and A and B are fit parameters.

rium value $n_c(x) = \alpha \mathcal{I}(x) / (1 + \alpha \mathcal{I}(x))$ or simply the value attained by $t = 0$ when the switch-on was concluded. After inserting (13) into $\mathcal{A}(L, t) = (1/d_B) \int_0^L dx (1 - n_c(x, t))$, one obtains

$$\mathcal{A}(L, t) = \frac{L}{d_B} - \left(\frac{L}{d_B} - \mathcal{A}(L, 0) \right) e^{-t/\tau}, \quad (14)$$

where $\mathcal{A}(L, 0)$ is the absorption at $t = 0$. Experiments of Langhoff and Giesselmann¹⁴ revealed that both absorption and spontaneous polarization increase following monoexponential laws with the same characteristic times. In view of our relation (14) it is clear that this characteristic time for absorption should be equal to the thermal relaxation time τ . We have found, however, that a simple monoexponential law for the spontaneous polarization breaks down in the vicinity of the critical point, while it holds outside the critical region.

Given $n_c(x, t)$ is deeply buried in (12) the off-dynamics is not necessarily simple. However we can expand P_s^0 in (12) assuming that $n_c(x, t)\delta$ is small

$$\begin{aligned} \overline{P}_s(T, I_0, t) &= P_s^0 + T \frac{\partial P_s^0}{\partial T} \frac{\delta}{L} \int_0^L dx n_c(x, t) + \dots \\ &= P_s^0 + T \frac{\partial P_s^0}{\partial T} \frac{\delta}{L} e^{-t/\tau} \int_0^L dx n_c(x, 0) + \dots \\ &= P_s^0 + T \frac{\partial P_s^0}{\partial T} \left(1 - \frac{d_B}{L} \mathcal{A}^0 \right) e^{-t/\tau} \delta + O(e^{-2t/\tau}) \end{aligned} \quad (15)$$

where $\mathcal{A}^0 = \mathcal{A}(L, 0)$.

We have shown that $\overline{P}_s(T, I_0, t)$ has an expansion in $e^{-t/\tau}$. As more terms in the expansion are required to

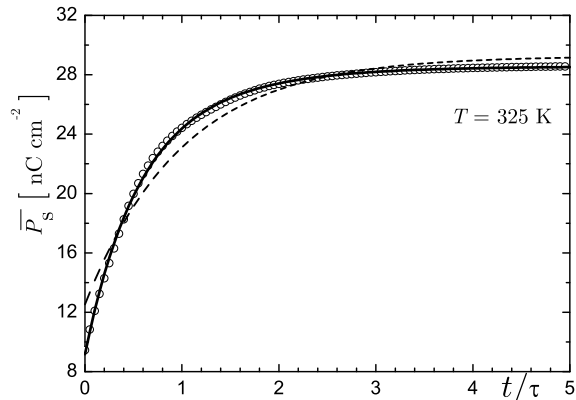


FIG. 7. The same as in Fig. 6, but for $T = 325$ K, closer to the critical temperature $T_{AC} \approx 327$ K. The data obtained by using formula (12) are presented by circles, monoexponential fit by the dashed line, and biexponential fit of the form $A + Be^{-t/\tau} + Ce^{-2t/\tau}$ by the solid line.

describe $P_s^0(T/(1-n_c\delta))$ more precisely, then so are faster decay terms $e^{-2t/\tau}$, ... represented. Unfortunately, coefficients of this expansion are not available from existing experiments, so we tried to fit time-dependent polarization with the simple form $\overline{P}_s = A + Be^{-t/\tau} + Ce^{-2t/\tau}$, with A , B and C being the fit parameters. One can see that the monoexponential form ($C = 0$) works fairly well outside of the critical region (Fig. 6), but not so well in the vicinity of the critical point (the dashed line in Fig. 7). If one uses the biexponential form, $C \neq 0$, the fit becomes much better (Fig. 7).

IV. SUMMARY AND OUTLOOK

We have argued, given light is absorbed in driving the photoferroelectric effect, that the mechanism and details of absorption are crucial to understanding the optical depression of electric polarization. To achieve a polarization response to illumination, the ground state population of dye molecules has to be materially changed. From this it follows that the intensity profile is non-Beer (non-exponential). Equally there must be a characteristic dynamics for the switch-on phase where a front of dye depletion progresses through the thickness. Non-uniformity of the polarization means that measurements of the depres-

sion must underestimate depression assuming a uniform intensity I_0 through the sample. This underestimate has implications for modeling the balance of primary and secondary influences in the photoferroelectric effect.

Future experiments should simultaneously measure the absorption in detail, namely the Beer length d_B for weak illumination and the nonlinear absorption in more intense cases to yield the effective incident intensity (our quantity α). Thereby only one parameter would remain, our δ , which is a measure of how much the ordering effect of a dye molecule is lost when it is bent (on entering the *cis* state).

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